General Disclaimer

One or more of the Following Statements may affect this Document

- This document has been reproduced from the best copy furnished by the organizational source. It is being released in the interest of making available as much information as possible.

- This document may contain data, which exceeds the sheet parameters. It was furnished in this condition by the organizational source and is the best copy available.

- This document may contain tone-on-tone or color graphs, charts and/or pictures, which have been reproduced in black and white.

- This document is paginated as submitted by the original source.

- Portions of this document are not fully legible due to the historical nature of some of the material. However, it is the best reproduction available from the original submission.

STATISTICAL THEORY OF THE

INHOMOGENEOUS ELECTRON GAS

DISSERTATION

Presented in Partial Fulfillment of the Requirements for
the Degree Doctor of Philosophy in the Graduate
School of The Ohio State University

By

John R. Smith, B. S. E. P.

* * * * * *

The Ohio State University
1968

Approved by

Adviser

Department of Physics
and Astronomy

ACKNOWLEDGEMENTS

The author wishes to express his gratitude to Professor J. Korringa, under whose direction this work was carried out. Also, the author is thankful for the support and hospitality provided by the National Aeronautics and Space Administration. In particular, Mr. R. Breitwieser of NASA was most cooperative. Finally, the author is deeply indebted to his wife, Norma Jean, whose patience, encouragement, and good nature made this work possible.

VITA

[redacted] Born - [redacted]

1962.....	B.S.E.P., Toledo University, Toledo, Ohio
1962-63.....	Mershon Fellow, The Ohio State University, Columbus, Ohio
1963-64.....	Teaching Assistant, Department of Physics, The Ohio State University, Columbus, Ohio
1964-65.....	Fellow, The Ohio State University, Columbus, Ohio
1965-Present..	Research Scientist, N.A.S.A., Cleveland, Ohio

PUBLICATIONS

"Theoretical Study of Zero-Field Electron Work Function of Metal Immersed in Gas - Direct Application to Cesium Thermionic Diode", K. P. Luke and J. R. Smith, NASA TN D-2357, July 1964.

FIELDS OF STUDY

Major Field: Physics

Minor Fields: Engineering and Mathematics

TABLE OF CONTENTS

LIST OF TABLES

LIST OF ILLUSTRATIONS

CHAPTER I

INTRODUCTION

The wealth of experimental data available today on electronic work functions of bare metal surfaces[1] is not at all matched by theoretical calculations of same. In fact, the total electron work function has been calculated from first principals for only one metal, Na, in a classic work by Bardeen.[2]

There have been numerous empirical correlations made relating the electron work function of metals to atomic volume, compressibility, the first atomic ionization potential, the energy of the lattice, surface energy, and electronegativity. These efforts are enumerated by Samsonov et al[3] (see also Dobretsov et al[4]).

But the initial step towards a calculation of work function was made by Wigner and Bardeen.[5] They showed that the work function can be broken up into two parts, the first depending on bulk properties of the metal and the second representing the effect of the electrical double layer formed at the surface. Wigner and Bardeen then calculated semiempirically the part of the work function depending on bulk properties for the alkali metals.

Herring[6] reviews the subsequent efforts through 1949 to calculate the electron work function. Calculations made after 1949 are reviewed in the remainder of this paragraph. Oldekop and Sauter[7] attempted to calculate the correlation energy contribution to the work function. They assume the charge density distribution is given correctly by the Thomas Fermi equation, and then calculate the electric field due to the deficiency of electrons around the electron that is to be removed. They find that their "polarization" interaction is almost as large as the experimental work function for the alkali metals. They could have much more easily (and more accurately), made use of Wigner's interpolation formula[8] for the correlation energy and Koopmans's theorem[9] to arrive at the above conclusion immediately. A semiempirical calculation of the double layer of metallic surfaces using a one electron scheme was performed by Garron.[10] M. Kaplit[11] computed the effect of grain orientation on the surface dipole layer of tungsten in the presence of extremely high electric fields (0.1 to 10 V/Å), and under zero field conditions. Although he included both correlation and exchange energies, his results were disappointing. He found it necessary to assume 0.3 free electrons per atom under the zero field condition and 0.95 free electrons per atom under the high field condition in order to obtain the correct work function differences between grain orientations. These values are of course not consistent with each other and certainly not with the valence of the

tungsten atom, which is 6. It is felt here that the main source of his inaccuracy was the use of the Weizsäcker[12] inhomogeneity correction. The coefficient of this term has been shown to be nine times too large,[13] and one would expect that grain orientation effects would depend heavily on inhomogeneity expressions. Still, this is an important work since it is the only effort to include exchange and correlation energies in grain orientation studies that exists. Finally, Dubjko et al[14] claim to have calculated the part of the work function depending on bulk properties of the metals with atomic numbers below 40. However, their scheme obviously is not applicable to metals since they find it necessary to assume that the removal of an electron from a metal is equivalent to removal of that electron from a given metal cell (Wigner and Seitz Polyhedron[15]), without disturbing any of the other cells. But valence electron wave functions are not localized in any one cell, and are in fact spread out over many cells. In the free electron model, on which they claim their theory is based, the valence electron wave functions are spread throughout the entire metal.

This concludes a review of electron work function theories. In summary, a self-consistent many electron calculation of the electron work function including exchange and correlation energies in computing bulk and/or surface contributions has been done[2] for only one metal, Na.

Another quantity which characterizes the surface region of a metal is the surface potential. Experimental and theoretical efforts to determine this quantity are reviewed by Herring et al,[16] Juretschke,[17] Bardeen,[18] and Gerstner.[19]

The most sophisticated calculation of the surface potential was done by Loucks and Cutler.[20] They use a Bohm Pines formalism to calculate the one-electron potential energy in the surface region of Na for a number of values of screening parameter. However, complexity forces them to make the following assumptions among others: first, they neglect the effect of the electrical double layer, and secondly they place an infinitely high potential barrier at the surface in order to obtain wave functions. It is seen later that the first approximation may not be too damaging in the case of Na, but would certainly not be useable for the higher electron density metals. The second approximation of course makes self consistency impossible.

A third quantity of interest in surface physics is the surface energy. A number of thorough reviews of experimental and theoretical determinations of this quantity for metal surfaces are available.[21-25] It is best to start with a quote from Semenchenko,[25]

> We consider it necessary, however, to emphasize once more that at the present time a reliable test of both theoretical and empirical formulae is impossible on account of a lack of experimental data.

With the preceding sobering and not always mentioned thought in mind, let us note first that empirical theories of surface energy are at present enjoying considerably better agreement with experimental data then are the more basic calculations.[26,27] A rule of thumb for calculating surface energies was put forward by Sugiyama[28] which is fairly accurate but at present lacks theoretical justification. The most successful theory to date is that of Zadumkin.[29] He assumed the number density distribution of electrons at a metal surface can be adequately represented by the Thomas Fermi result. Then including exchange, correlation, and Weizsäcker energies, he calculated surface energies on a one dimensional model. He made a number of corrections, in addition, so that his one dimensional scheme might tend to better describe a three dimensional reality.

This completes the review of background material pertinent to this thesis. It will now be made explicit just what is desired to be calculated here. The metals to be studied will be the alkali metals, the noble metals, Mg, Al, and selected transition metals. For these metals a self consistent calculation of the electron work function will be made. This will be a many electron theory which will include exchange and correlation energies in computing self consistently both the bulk and surface contributions to the work function. In addition, electron number density distributions and the potential energy of an electron at the top of the Fermi distributions will be computed and plotted in the sur-

face region. The potential energy will be self consistent and will include coulomb as well as exchange and correlation potential energies. Lastly, primarily for purposes of comparison with the only available calculation of this type[2] and for further clarification of the model, the surface energy will be calculated. The surface energy calculation will be a self consistent many electron scheme.

For all of the above computations, only quantities available from the periodic table will be used. This necessitates a rather crude model, that used by Bardeen[2] and described in section IV.

The method used will be a statistical theory of an inhomogeneous electron gas. There has been much use of statistical schemes in nuclear, atomic, molecular, and solid state physics, and considerable improvement of the method since Thomas[30] and Fermi[31] brought it forth 41 years ago. Two complementary reviews of the statistical approximation in quantum mechanics are available, the first by March[32] and the second by Gombas.[33] Recently, there have been important advances made in terms of systematically improving the accuracy of the statistical theory of the inhomogeneous electron gas. In the Hartree Fock approximation, three authors[13, 34, 35] have by seemingly independent schemes used expansions in powers of $\hbar$ to obtain identical inhomogeneity and exchange corrections to the Thomas-Fermi energy. The exchange correction is identical with that first proposed by Dirac,[36] and the inhomogeneity correction is of the same

form as that proposed by Weizsäcker[12] but has a coefficient 1/9 as large. Although their Thomas-Fermi equations with quantum corrections have been found to be unreliable,[37] their total energy expression[38, 40] and electron number density distributions obtained by applying a variational scheme to it have shown phenomenal improvement over uncorrected values. Schey et al[37] propose that the reason for this is that while they suspect the expansion for the density is asymptotic, they feel the energy expansion is less asymptotic since it is an integral of products of density expansions.

Other suggestions have been offered[41, 42] for improvements to the Thomas Fermi equation. But a very powerful and general statistical theory was introduced by Hohenberg and Kohn[43] (HK), in 1964 which provides a legitimate basis for many of the ad hoc schemes of the past and for making systematic corrections to them. In their theory correlation effects come in quite naturally. They prove that the ground state energy of an interacting inhomogeneous electron gas in a static potential $v(\underline{r})$ can be written in the form

$$E_v[n] = \int v(\underline{r})\, n(\underline{r})\, d\underline{r} + \tfrac{1}{2} \int \frac{n(\underline{r})\, n(\underline{r}')}{|\underline{r} - \underline{r}'|}\, d\underline{r}\, d\underline{r}' + G[n(\underline{r})] \tag{1.1}$$

where $n(\underline{r})$ is the electron density and $G[n]$ is a universal (valid for any number of particles and any external potential), functional of the

density. They show, moreover, that the above expression is a minimum for the correct density function $n(\underline{r})$. Thus it remains to find the function G in order to be able to describe quite general inhomogeneous systems.

HK determine G[n] for two cases: first, for a gas of almost constant density, and secondly for the case of a slowly varying, but not necessarily almost constant density. The latter scheme is what we will make use of in the surface region of metals. For slowly varying densities, HK write G[n] with some confidence in terms of a gradient expansion as follows:

$$G[n] \equiv \int g_2[n]\, d\underline{r} \tag{1.2}$$

where

$$g_2[n] = g_0(n(\underline{r})) + \sum_{i=1}^{3} g_i(n(\underline{r}))\cdot \nabla_i n(\underline{r}) + \cdots \tag{1.3}$$

and where

g_0 = kinetic + exchange + correlation energy density of a uniform gas of density $n(\underline{r})$.

Fortunately, the theory of uniform electron gases has progressed considerably and there are a number of interpolation formulae available for the correlation energy density of a uniform electron gas.[44, 45] It should be noted, however, as HK point out, that as

such the above gradient expansion does not include quantum density oscillations such as Friedel oscillations or atomic shell structure. In addition, they show that there are no terms containing odd orders of $\nabla_i n$ since $g_r[n]$ must be invariant under rotations about $\underline{r}$. Therefore,

$$g_r[n] = g_0(n(\underline{r})) + g_2^{(2)}(n)\,\underline{\nabla} n \cdot \underline{\nabla} n + \cdots \tag{1.4}$$

Then using a random-phase expression for the electronic polarizability, HK determine that

$$g_2^{(2)} = 1/72n \tag{1.5}$$

which is exactly the coefficient derived in the Hartree Fock scheme by Kompaneets, et al[13, 34, 35].

Up to now we have not worried about the existence of convergence of the gradient expansion. Fortunately, HK did worry about this.[46] They note that in general the series does not strictly converge. But they expect it to be of some utility for sufficiently small values of $|\underline{\nabla} n|/n$. It is not unusual that a divergent infinite series may be of some use in physics. For instance it is found at time that the first few terms of a diverging series give quite useful answers. For a mathematical introduction to this see Erdelyi's[47] book. For a physical example of this see Kaempfler.[48]

It is a simple matter to show that, e.g., for Bardeen's resultant $n(\underline{r})$, relation (81) of H. K. is not satisfied, and thus in this case the gradient expansion does not converge.

So we have a situation here which is uncomfortable, but not fruitless. Keeping only the first term g_0 on the right in equation (1.5), we have a scheme which was first suggested by Gombas[49] and later extended by Lewis[41] and Erma.[50] This scheme has been quite useful.[50, 55] Also, as mentioned earlier, inclusion of the next term[38, 39] as derived using the RPA (see eq. (1.5)), can lead to noticeable improvement, at least in the Hartree Fock approximation. Further, Kohn and Sham[51] have developed a statistical theory based on the gradient expansion which includes quantum density oscillations. This was applied to atoms by Tong and Sham.[52] Quite accurate values for energies and electron number densities were obtained and, as expected, the shell structure was reproduced. For completeness it should be mentioned that Kohn and Sham have extended these ideas to include the possibility to compute single-particle-like excitations.[53, 54]

Thus the ground work is now laid so that the remaining chapters can be previewed. As mentioned earlier, it is desired to calculate metal surface properties. Thus in Chapter II the applicability to metal surface physics of the homogeneous scheme, i.e., of keeping only g_0 in equation (1.4), is evaluated. We try this first because it is a very simple scheme which has met with success in other areas.[50, 55] Chapter III is devoted to the description of $g_2^{(2)}$ (eq. (1.5)). That is, it is determined there what part of the first inhomogeneity correction is kinetic energy and what part is potential

energy. This information is useful in defining a one-electron potential energy. Chapter IV gives the quantitative application of the statistical theory to a number of metals.

CHAPTER II

SOME GENERALITIES AND LIMITATIONS OF THREE COMMON APPROXIMATIONS TO THE STATISTICAL THEORY OF THE ELECTRON GAS

Despite the successes previously mentioned of statistical theories which neglect inhomogeneity corrections, there are some areas to which they do not apply. For instance, Balazs[56] showed that these types of theories will never describe a stable molecule or molecular ion. But it is being used at present in metal surface physics.[57]

Thus it appears that a basic investigation of its applicability in predicting the dependence of the electron work function on metal surface properties is in order. It will be shown below that the theory predicts that the electron work function is independent of the system. Experimentally, it is well known that the electron work function is strongly dependent on surface grain orientation, on the amount and kind of impurities absorbed on the surface, and on the substrate species. The basis for this shocking failure will be shown to be the requirement of finite domain for systems described by this theory.

It is general practice to limit electron density distributions to finite domains when treating them with the statistical approximation neglecting inhomogeneity corrections.[58] However, a general proof of

the necessity of a finite domain has never been offered.* It will now be shown that at least certain of these schemes must be limited to a finite domain and the boundary electron density will be found. The proof will be made for a general three-dimensional electron gas, but the interpolation formula of Wigner as corrected by Pines[60] for the correlation energy will be used since it is desired to apply the result to metal surface physics. From equations (1.1) and (1.3), we have in this scheme (hereafter referred to as T. F. D. G. for Thomas Fermi Dirac Gombas).

$$E_v[n] = \int\left[\chi_K n^{5/3} - \chi_A n^{4/3} - \frac{\gamma_1 n^{4/3}}{\gamma_2 + n^{1/3}}\right] d\underline{r} + \frac{1}{2}\iint \frac{n(\underline{r})n(\underline{r}')}{|\underline{r}-\underline{r}'|} d\underline{r}\, d\underline{r}' + \int v(\underline{r})n(\underline{r})\, d\underline{r} \qquad (2.1)$$

where

$\chi_K = 3/10(3\pi^2)^{2/3}$ = kinetic energy coefficient

$\chi_A = \frac{3}{4}\left(\frac{3}{\pi}\right)^{1/3}$ = exchange energy coefficient

$\gamma_1 = 0.056$ = correlation energy coefficient

$\gamma_2 = 0.079$ = correlation energy coefficient,

and atomic units are used.

---

*The closest anyone has come to a general proof is the thinking offered by Sheldon.[59] Neglecting correlation energies, he proved that neutral and positively charged systems must be limited to a finite domain. He also found the boundary density under the assumption that it is independent of position again neglecting correlation energies.

The energy minimization principal of HK[62] yields

$$\frac{\delta}{\delta n}\left\{E_v[n] - \mu \int n(\underline{r})\, d\underline{r}\right\} = 0 \qquad (2.2)$$

or,

$$5/3\, \chi_K\, n^{2/3} - 4/3\, \chi_A\, n^{1/3} - \frac{\gamma_1 (n^{2/3} + 4/3\, \gamma_2\, n^{1/3})}{(\gamma_2 + n^{1/3})^2} + $$

$$+ (\varphi - \mu) = 0 \qquad (2.3)$$

where

$$\varphi(\underline{r}) = v(\underline{r}) + \int \frac{n(\underline{r}')}{|\underline{r} - \underline{r}'|}\, d\underline{r}'$$

Rewriting equation (2.3) one obtains

$$5/3\, \chi_K\, n^{2/3} + \left\{-4/3\left[\chi_A + \frac{\gamma_1 \gamma_2}{(\gamma_2 + n^{1/3})^2}\right]\right\} n^{1/3} +$$

$$+ \left[-\frac{\gamma_1\, n^{2/3}}{(\gamma_2 + n^{1/3})^2} + \varphi - \mu\right] = 0 \qquad (2.4)$$

or,

$$n^{1/3} = \nabla_0^{1/3}\left(f \pm \sqrt{f^2 - \varphi + \mu + g}\right) \tag{2.5}$$

where

$$\nabla_0 = \left(3/5 x_K\right)^{3/2}$$

$$f = \left\{ \frac{4\left[x_A + \frac{\gamma_1 \gamma_2}{(\gamma_2 + n^{1/3})^2}\right]^2}{15\, x_K} \right\}^{1/2}$$

$$g = \frac{\gamma_1 n^{2/3}}{(\gamma_2 + n^{1/3})^2}$$

It remains to choose the sign in equation (2.5). First, from physical reasoning one would expect n to be continuous within the domain of the system. Thus, if there is to be a sign change at some point on the R.H.S. of equation (2.5), it must occur on the closed surface where

$$f^2 - \varphi + \mu + g = 0 \tag{2.6}$$

or

$$n^{1/3} = \nabla_0^{1/3} f \tag{2.7}$$

But n must be real to be physically meaningful. Hence, everywhere on the aforementioned surface the following equation must hold

$$\underline{\nabla}(f^2 - \varphi + \mu + q) \cdot \underline{n} = 0 \qquad (2.8)$$

where

$\underline{n} \equiv$ unit vector normal to the surface

There are, in fact, three roots to equation (2.7). Two are complex and one is real. The two complex roots are, of course, nonphysical and the one real root is 0.12.

Hence, we have two equations (eqs. (2.6) and (2.8)), and three unknowns (x, y, and z). In general, two equations containing three unknowns can be satisfied on a line only. But if the sign in equation (2.5) is to change on a line in space, then n cannot be continuous (the + and - regions have to be separated by a surface to maintain continuity).

However, one might ask whether the mathematically remote conditions for the existence of this branching surface are as remote physically. To answer this, consider an atom or a system of atoms as in a solid or gas. Near the nuclei, $-\varphi$ becomes very large and positive so that the plus sign must be used in equation (2.5) in order for $n^{1/3}$ to be positive. Thus it is some distance from the nuclei before there is any possibility of existence of a branching surface. But equation (2.8) states that $\underline{\nabla}\,\varphi \cdot \underline{n} = 0$ everywhere on this surface.

The statement is exact when correlation energies are neglected and is true to a good approximation[33] when correlation energies are included. Additionally, one obtains from equation (2. 6) that

$$-\varphi = (f^2 + g)_{n^{1/3}=0.12}$$

everywhere on this surface ($\mu = 0$ so that $n \to 0$ at large distances).

In summary, one obtains that the physical conditions necessary for the branching surface to exist are:

1. The system must be negatively charged.

2. There must be a surface surrounding all the nuclei everywhere on which $n^{1/3} = 0.12$ and the potential is $(f^2 + g)_{n^{1/3}=0.12}$ and the electric field is zero.

Thus one can see that a system for which the branching surface can exist is a very special one indeed.

Thus, in general, one must choose one sign and use it for the entire domain of the system. The choice must be the positive sign so that n will be positive in region where φ becomes very large (e. g. , in the region near the nucleus of an atom). Also, a positive sign must be chosen so that equation (2. 5) gives a positive n when exchange and correlation energies are small or neglected, on the basis of the correspondence principal. Therefore,

$$n^{1/3} = \nabla_0^{1/3}\left(f + \sqrt{f^2 - \varphi + \mu + g}\right) \tag{2.9}$$

Since $\partial f/\partial n^{1/3} < 0$, it is clear from equation (2.9) that the smallest value that n can take which satisfies same is a root of equation (2.7), which we have seen to be 0.12. Therefore,

$$n^{1/3} > 0.12 \tag{2.10}$$

But any physical system has a finite number of electrons. Therefore, from equation (2.10) T. F. D. G. systems must have a finite domain. Of course, the same conclusion can be made for T. F. D. systems.

Now let us see what the boundary value of n is. As mentioned in Chapter I, HK show that the energy functional E (eq. (1.1)), assumes its minimum value for the correct $n(\underline{r})$, if the admissible functions are restricted by the condition

$$N[n] = \int n(\underline{r})\, d\underline{r} = N. \tag{2.11}$$

Thus we must choose the domain of the system as well as the distribution within the domain to be such that the energy functional is minimized. The approach that we will follow is similar to that used by Sheldon, [59] except that we will not assume that the boundary density is independent of position and will include correlation energies. †

---

† Boundary values have been found only by Gombas, [23] Bonet and Bushkovitch, [62] and Sheldon. [59] Gombas has only considered spherically symmetric systems and obtained only an approximate value when correlation energies were included. Bonet and Bushkovitch's assumptions were more restrictive than Sheldon's (see preceding footnote).

Let the distribution which minimizes E be confined within the volume V. Now, let us consider another distribution which also satisfies equations (2. 11) and (2. 2), and which is confined within the volume V + dv, where dv an <u>infinitesimal</u> increment in V. Let

$$E_V^* \equiv \int_V \left(\chi_K n^{*5/3} - \chi_A n^{*4/3} - \frac{\gamma_1 n^{*4/3}}{\gamma_2 + n^{*1/3}} \right) d\underline{r} + \frac{1}{2} \int_V \int_V \frac{n^*(\underline{r}) n^*(\underline{r}')}{|\underline{r} - \underline{r}'|} d\underline{r}\, d\underline{r}' + \int_V v(\underline{r}) n^*(\underline{r})\, d\underline{r} \tag{2.12}$$

and

$$E_v^* \equiv \int_{dv} \left(\chi_K n^{*5/3} - \chi_A n^{*4/3} - \frac{\gamma_1 n^{*4/3}}{\gamma_2 + n^{*1/3}} \right) d\underline{r} + \int_{dv} \int_V \frac{n^*(\underline{r}) n^*(\underline{r}')}{|\underline{r} - \underline{r}'|} d\underline{r}\, d\underline{r}' + \frac{1}{2} \int_{dv} \int_{dv} \frac{n^*(\underline{r}) n^*(\underline{r}')}{|\underline{r} - \underline{r}'|} d\underline{r}\, d\underline{r}' + \int_{dv} v(\underline{r}) n^*(\underline{r})\, d\underline{r} \tag{2.13}$$

where the starred quantities refer to values obtained with a volume of V + dv, and where

$$E^* = E_V^* + E_v^* \tag{2.14}$$

Since $n(\underline{r})$ satisfies equation (2.2) within the volume V, one obtains

$$E_V - E = \mu \frac{\delta}{\delta m} \int_V n(\underline{r})\, d\underline{r} = -\mu \int_{dv} n^*(\underline{r})\, d\underline{r} \tag{2.15}$$

But for the correct $n(\underline{r})$ we have, following HK,

$$E^* - E = 0$$

Therefore

$$E_V^* + E_v^* - E = -\mu \int n^*(\underline{r})\, d\underline{r} + E_v^* = 0$$

or

$$\int_{dv} \left(-\mu n^* + \chi_K n^{*5/3} - \chi_A n^{*4/3} - \frac{\gamma_1 n^{*4/3}}{\gamma_2 + n^{*1/3}} + \phi^* n^* \right) d\underline{r} =$$

$$= \tfrac{1}{2} \int_{dv} \int_{dv} \frac{n^*(\underline{r}) n^*(\underline{r}')}{|\underline{r} - \underline{r}'|}\, d\underline{r}\, d\underline{r}'$$

(2.15)

Since dv is an infinitesimal volume, one can, in the spirit of differential calculus, neglect the R.H.S. of equation (2.15). Combining this with the fact that n* must satisfy equation (2.2), one obtains

$$\int_{dv} \left[-2\chi_K n^{*5/3} + \chi_A n^{*4/3} + \frac{\gamma_1 \gamma_2 n^{*1/3}}{(\gamma_2 + n^{*1/3})^2} \right] d\underline{r} = 0 \qquad (2.16)$$

Equation (2.16) is a perfectly general equation for determine the boundary density of any T.F.D.G. statistical system. If a correlation energy expression other than Wigner's is desired to be used, arriving at an equation corresponding to equation (2.16) would be quite straightforward, with only the third term in the brackets being different.

Again, according to HK (eq. (2.2)), the energy functional is to be minimized with respect to <u>all</u> small variations from the correct $n(\underline{r})$, provided equation (2.11) is satisfied. Thus, one is free to choose

$$dv = r^2 \sin\theta \, d\phi \, d\theta \, dr$$

for all coordinates r, θ, and ϕ of the bounding surface. Thus equation (2.16) implies

$$\left\{-2\chi_K n^{5/3}(r,\theta,\phi) + \chi_A n^{4/3}(r,\theta,\phi) + \right.$$

$$\left. + \frac{\gamma_1\gamma_2 n^{4/3}(r,\theta,\phi)}{\left[\gamma_2 + n^{1/3}(r,\theta,\phi)\right]^2} \right\} r^2 \sin\theta \, d\phi \, d\theta \, dr = 0$$

for all coordinates r, θ, and ϕ of the bounding surface. Therefore,

$$-2\chi_K n^{5/3} + \chi_A n^{4/3} + \frac{\gamma_1\gamma_2 n^{4/3}}{(\gamma_2 + n^{1/3})^2} = 0 \qquad (2.17)$$

The root n = 0 is thrown out, since it has been shown that $n > 0$ (see eq. (2.10)). Thus, it remains to solve the equation

$$n + \left(2\gamma_2 - \frac{\chi_A}{2\chi_K}\right) n^{2/3} + \left(\gamma_2^2 - \frac{\gamma_2 \chi_A}{\chi_K}\right) n^{1/3} -$$

$$- \frac{\chi_A \gamma_2^2 + \gamma_1\gamma_2}{2\chi_K} = 0 \qquad (2.18)$$

Equation (2.18) has three roots, two of which are complex and hence thrown out. The real root is

$$n_b^{1/3} = 0.14 \qquad (2.19)$$

Thus the boundary density for all T. F. D. G. systems is the same and is in fact independent of position on the boundary.

In like manner, neglecting correlation energies ($\gamma_1 = \gamma_2 = 0$), one finds (commonly called the T. F. D. scheme),

$$n_b^{1/3} = \frac{\chi_A}{2\chi_K} = 0.128,$$

and neglecting correlation and exchange energies (Thomas Fermi approximation), one obtains

$$n_b^{1/3} = 0$$

as expected.

Let us now apply the above result to a calculation of the dependence of electron work function, ϕ_e, on surface properties of metals. The electron work function is defined as[2]

$$\phi_e = -\left(\frac{\partial E}{\partial N}\right)_0 \tag{2.20}$$

where the subscript 0 is used to indicate that the net charge of the system is zero.

As pointed out by Hulthen[63] equation (2.2) implies that

$$\mu = \partial E / \partial N$$

therefore

$$\phi_e = -\mu \tag{2.21}$$

Thus, if ϕ_e is to depend on surface properties, then μ must depend on them. From equation (2.3), one has

$$-\phi_e = \mu = \phi_b + \tfrac{5}{3} \chi_K n_b^{2/3} - \tfrac{4}{3} \chi_A n_b^{1/3} - \frac{\gamma_1 \left(n_b^{2/3} + \tfrac{1}{3} \gamma_2 n_b^{1/3} \right)}{\left(\gamma_2 + n_b^{1/3} \right)^2} \qquad (2.22)$$

where the subscript b indicates value on the boundary of the system, as before.

It is clear, then, that the boundary of the system represents an equipotential surface. Thus, as pointed out by Sheldon,[64] since the system is neutral and since there is no charge outside the system, ϕ = constant on and outside the boundary.

But we are free to set arbitrarily $\phi = 0$ at an infinite distance from the system. Then nothing on the R.H.S. of equation (2.22) depends on surface properties, and therefore the electron work function is independent of the physical system in the T. F. D. G. scheme or the T. F. D. scheme.

It will be seen that this disappointing result does not mean that statistical theories in general are not useful in surface physics. Some indication of the direction to go next is indicated by Balazs,[56] who showed that the addition of the first inhomogeneity correction yields stable homonuclear, diatomic molecules at least.

There are, however, two available ways to include the first inhomogeneity correction. That is, one could turn to the expansion[13, 34, 35] schemes for n or to a direct variational method.[38, 40] Both theories apparently satisfy formally the postulates of HK enumerated in Chapter I. But the former method has been found lacking,[37] and, in fact it can be easily shown that it will also predict that φ_e is independent of the physical system. To see this, let us look at equation (16) of reference 34 for the case of a neutral metal. Should one choose the arbitrary constant in the potential energy so that the latter vanishes at infinity, then in order for the electron number density to vanish at infinity the constant E_o must be zero, as pointed out by Kirzhnits[34]. But Kirzhnits shows that E_o is the energy of the maximum filled level. Thus it is clear that the expansion schemes for μ predict that the electron work function is zero, even when the first inhomogeneity correction is included.

So we are left with the direct variational method. To intelligently apply this method, however, it will be shown to be useful to know what part of the first inhomogeneity correction is kinetic energy, and what part is potential energy (see equations (3. 2) and (3. 6)).

CHAPTER III

EVALUATION OF THE FIRST INHOMOGENEITY CORRECTION TO THE POTENTIAL ENERGY AND THE CORRESPONDING ONE-ELECTRON POTENTIAL CONTRIBUTION

It is desired in this chapter to consider the first inhomogeneity correction, $\int g_2^{(2)}(n) \mid \underline{\nabla} n \mid^2 d\underline{r}$. It will be determined here what part of this term is kinetic energy and what part is potential energy.

But before beginning this derivation, let us make clear the value of knowing the potential energy contribution of the first inhomogeneity contribution. It will be seen that it can be used in a one-electron formulation of the many-electron problem.

The one-electron formalism has been much used in the description of atoms and solids. It has been the basis of, e.g., the band theory of solids, the central field approximation of atomic physics, and the surface potential at a metal surface.

Attempts have been made[65] to determine under what conditions a general set of equations such as the Hartree Fock equations is a scheme in which each electron moves in the same potential.

Recently, Kohn and Sham[66] (KS) have succeeded in formally replacing the many-electron problem by an exactly equivalent set of

self-consistent one electron equations. To do this, they make use of the theory of HK expounded in Chapter I of this thesis. They note that $G[n]$ can be written as

$$G[n] \equiv T_s[n] + E_{xc}[n]$$

where $T_s[n] \equiv$ kinetic energy of a system of noninteracting electrons with density $n(\underline{r})$ (it follows from the theory of HK that it can be written as a universal functional of the density), and $E_{xc}[n] \equiv$ exchange + correlation energies of an interacting system with density $n(\underline{r})$.

Then from equation (2.2), one obtains

$$\int \delta n(\underline{1}) \left\{ -\mu + \varphi(\underline{1}) + \frac{\delta T_s[n]}{\delta n(\underline{1})} + \frac{\delta E_{xc}[n]}{\delta n(\underline{1})} \right\} d\underline{1} = 0 \qquad (3.1)$$

KS point out that the above equation is exactly the same as one would obtain for a system of noninteracting electrons, moving in the potential $\delta E_{xc}[n]/\delta n(\underline{r})$. Thus the $n(\underline{r})$ which satisfies the equation (3.1) also satisfies

$$\left\{ -\tfrac{1}{2}\nabla^2 + \left[\varphi(\underline{1}) + \delta E_{xc}[n]/\delta n(\underline{1}) \right] \right\} \psi_i(\underline{1}) = \epsilon_i \psi_i(\underline{1}) \qquad (3.2)$$

with

$$n(\underline{1}) = \sum_{i=1}^{N} |\psi_i(\underline{1})|^2 .$$

Thus, as promised, KS have shown that the many-electron problem is exactly equivalent to a set of one-electron equations.

But as before, it remains to find $E_{xc}[n]$. In the spirit of HK's gradient expansion, they expand $E_{xc}[n]$ and $T_s[n]$ as

$$E_{xc}[n] = \int \epsilon_{xc}[n]\, n\, d\underline{r} + \int \epsilon_{xc}^{(2)}(n) |\nabla n|^2 d\underline{r} + \cdots \quad , \tag{3.3}$$

$$T_s[n] = \int \frac{3}{10} (3\pi^2 n)^{2/3} n\, d\underline{r} + \int t^{(2)}(n) |\nabla n|^2 d\underline{r} + \cdots , \tag{3.4}$$

where

$$\left.\begin{aligned} g_0[n] &= \left[\tfrac{3}{10}(3\pi^2 n)^{2/3} + \epsilon_{xc}(n)\right] n \\ g_2^{(2)}[n] &= \epsilon_{xc}^{(2)}(n) + t^{(2)}(n) \end{aligned}\right\} \tag{3.5}$$

consistent with equation (1.4).

Of course, $\epsilon_{xc}(n)\, n \equiv -\frac{3}{4}\left(\frac{3}{\pi}\right)^{1/3} n^{4/3} + \epsilon_c(n(\underline{r}))\, n$ where $\epsilon_c(n(\underline{r}))\, n \equiv$ correlation energy density of a uniform electron gas of density n.

As pointed out earlier, ϵ_c is a reasonably well known quantity.[44, 45] Thus HK note that when one can neglect or chooses to omit all but the first term on the R.H.S. of equation (3.3), then the one-electron potential is a known quantity

$$-\left(\frac{3}{\pi}\right)^{1/3} n^{1/3} + \frac{d}{dn}\left(n \epsilon_c(n)\right).$$

The contribution that will be made here is that the term $\epsilon_{xc}^{(2)}(n) |\nabla n|^2$ will be found, and its contribution to the one-electron potential,

$$\frac{d}{dn}\left[\epsilon_{xc}^{(2)}(n) |\nabla n|^2\right], \tag{3.6}$$

will also be found.

The result will be obtained under the assumption that HK's random-phase expression for $g_2^{(2)}$ is valid as given by equation (1.5). However, should a more accurate expression become available at a later date, a similar proof could be carried through.

A comparison of Kirzhnits'[32] first inhomogeneity term in his expansion in powers of n of the Hartree total energy and that in Eq. (2.2b) shows that they are identical. Thus, the first inhomogeneity term contributes only to $T_s[n]$ in the RPA. So, to $O(|\nabla n|^2)$ in E_v,

$$\delta E_{xc}[n]/\delta n(\underline{r}) = -\left(\frac{3}{\pi}\right)^{1/3} n^{1/3} + \frac{d}{dn}\left(n \epsilon_c(n)\right),$$

within the R.P.A. of HK.

PAGES 30, 31, 32, 33, 34, 35 & 36 HAVE BEEN LEFT INTENTIONALLY BLANK.

CHAPTER IV

AN APPLICATION TO THE SURFACE REGION OF METALS

As promised in the introduction, the statistical theory of HK will be applied to the surface region of metals. The model used for the metal will be the same as that used by Bardeen,[2] the "jellium" model, as Herring[74] named it. This model has been much discussed in the literature.[17,74-77] It is a model in which the positive charge of the metal ions is replaced by a continuous charge density which is uniform over each cell. For bulk metal computations, this is more commonly known as the "Free Electron" model. The surface of this "jellium" is taken to be planar. Justification for this is that as pointed out by Kelley,[76] usually only the most energetic electrons have wave functions of periodicity at all comparable to that of the atoms in the surface plane. Thus it seems reasonable that the electron density generally will reflect only weakly the bumpiness of the atomic arrangement. However, it must be remembered that, e.g., electron work functions can vary by as much as several tenths of an electron volt with surface grain orientation. Also, one might be skeptical about applying this "Free Electron" model to other than

simple metals. However, recent experiments[78, 79] on the transition metal surfaces W, Re, and Mo indicate that even these metals, which have such complex bulk characteristics, are well represented at least for some surface properties by a "Free Electron" model in the surface region. The valence band, it is found, must be chosen wide enough to accomodate all the valence electrons. This is heartening news to the surface physicist since an overwhelming majority of the data in surface physics is taken on refractory metal surfaces.

Finally, a warning on the use of this model in the calculation of surface energies should be given. It has been pointed out by Herring[80] that it is not fair to compare the surface energy of a "jellium" metal with an actual metal of the same electron density. This is because the surface energy is defined to be the change in energy when the metal is cut in two, divided by the new area created. But Herring suggests that this chopping continue until cubes are formed which contain a charge equal to the number of valence electrons per atom of the actual metal. The amount of work done in separating these "jellium" atoms should approximate the cohesive energy of the metal. But especially the complex atoms obviously are not well represented by a uniform cube of positive charge. Herring points out through a simple-minded relation between energy of cohesion and surface energy that, because of this, even for the simple metal Na one would expect predicted surface energies to be too small by about a factor of 1/3.

Because grain orientation effects are not included here, it is felt justified to use the aforementioned "direct" scheme of HK (eq. (2.2)). It is to be remembered that this method does not include quantum oscillations but they should be an effect of the same order as grain orientation effects. If at a later date grain orientation effects are included, the considerable added complexity of HK's alternate scheme (eq. (3.2)), may be warranted.

Thus the formulation is hatched from equation (2.2). The correlation energy density in the surface regions of metals is represented[81, 82] by the interpolation formula of Wigner as corrected by Pines. Therefore,

$$E_v[n] = \tfrac{3}{10}(3\pi^2)^{2/3}\int n^{5/3}\,d\underline{r} + \int v(\underline{r})\,n\,d\underline{r} - \tfrac{3}{4}\left(\tfrac{3}{\pi}\right)^{1/3}\int n^{4/3}\,d\underline{r} + \tfrac{1}{2}\iint \frac{n(\underline{r})\,n(\underline{r}')}{|\underline{r}-\underline{r}'|}\,d\underline{r}\,d\underline{r}' - .056\int \frac{n^{4/3}\,d\underline{r}}{(.079+n^{1/3})} + \frac{1}{72}\int \frac{(\nabla n)^2}{n}\,d\underline{r} \qquad (4.1)$$

Combining equations (4.1) and (2.2), one obtains

$$\nabla^2 p = 18\left[\frac{(3\pi^2)^{2/3}}{2} p^{7/3} + (\phi - \mu)p - \left(\frac{3}{\pi}\right)^{1/3} p^{5/3} - \frac{5.6\times10^{-2} p^{7/3} + 4/3\,(4.4\times10^{-3})\,p^{5/3}}{(7.9\times10^{-2} + p^{2/3})^2}\right] \tag{4.2}$$

$$\nabla^2 \phi = 4\pi(n_+ \delta - n) \tag{4.3}$$

where

$$n \equiv p^2$$

$n_+ \equiv$ positive (jellium) charge density

$$\delta = \begin{cases} 1, & Z < 0 \\ 0, & Z > 0 \end{cases}$$

$z \equiv$ coordinate taken on an axis normal to the metal surface with

$z = 0$ at the surface

Since the jellium model is one-dimensional, equations (4.2) and (4.3) become

$$d^2p/dz^2 = 18\left[\frac{(3\pi^2)^{2/3}}{2} p^{7/3} + (\phi - \mu)p - \left(\frac{3}{\pi}\right)^{1/3} p^{5/3} - \frac{5.6\times10^{-2} p^{7/3} + 4/3\,(4.4\times10^{-3})\,p^{5/3}}{(7.9\times10^{-2} + p^{2/3})^2}\right] \tag{4.4}$$

$$\frac{d^2\phi}{dz^2} = 4\pi(n_+\delta - n) \tag{4.5}$$

It remains to solve equations (4.4) and (4.5) subject to the boundary conditions

$$\phi = 0, \quad z = +\infty$$

$$d^n\phi/dz^n = 0, \quad z = \pm\infty$$

$$\phi = \sqrt{n_+}, \quad z = -\infty \tag{4.6}$$

$$d^n\phi/dz^n = 0, \quad z = \pm\infty$$

where n = 1, 2, ...

The results of equations (4.4) and (4.5) can then be used to find the surface potential, $V^{(1)}$,

$$V^{(1)} = \phi - (3/\pi)^{1/3} n^{1/3} - \frac{.056n^{2/3} + .0059n^{1/3}}{(.079 + n^{1/3})^2} \tag{4.7}$$

and the surface energy ∇,

$$\nabla = \int_{-\infty}^{\infty} dz \left[\tfrac{3}{10}(3\pi^2)^{2/3}(n^{5/3} - n_+^{5/3}\delta) + \frac{(n - n_+\delta)}{2}\varphi + \right.$$
$$+ \tfrac{1}{72}(dn/dz)^2/n - \tfrac{3}{4}\left(\tfrac{3}{\pi}\right)^{1/3}(n^{4/3} - n_+^{4/3}\delta) -$$
$$\left. - \frac{5.6\times10^{-2} n^{4/3}}{7.9\times10^{-2} + n^{1/3}} + \frac{5.6\times10^{-2} n_+^{4/3}\delta}{7.9\times10^{-2} + n_+^{1/3}} \right]$$

(4.8)

$\nabla \equiv$ change in E when the jellium is cut in two ÷ new area formed, and the work function φ_e, $\varphi_e = -\mu$ (see eq. (2.21)).

From equation (4.4) and the boundary conditions (4.6), it is clear that

$$\varphi_e = -\varphi(-\infty) - \frac{(3\pi^2)^{2/3}}{2} n_+^{2/3} + \frac{5.6\times10^{-2} n_+^{2/3} + 5.9\times10^{-3} n_+^{1/3}}{(7.9\times10^{-2} + n_+^{1/3})^2} + \left(\frac{3}{\pi}\right)^{1/3} n_+^{1/3} \qquad (4.9)$$

Since our scheme does not include quantum oscillations, the following paramatized solution for n seems justified.

$$n = n_+ - \frac{n_+}{2} e^{\beta z}, \qquad z < 0$$

$$n = n_+/_2 e^{-\beta z}, \qquad z > 0 \tag{4.10}$$

One can then easily find the corresponding ϕ, using

$$\phi(z) = 4\pi \int_z^\infty (z_1 - z)(n - n_+ z)\, dz_1,$$

to yield

$$\phi = \frac{2\pi n_+ e^{\beta z}}{\beta^2} - \frac{4\pi n_+}{\beta^2}, \qquad z < 0$$

$$\phi = \frac{-2\pi n_+ e^{-\beta z}}{\beta^2}, \qquad z > 0. \tag{4.11}$$

It remains to find β. With our paramatized solution (4.10), we are assuming that the function which extremizes equation (4.1) belongs, to a good approximation, to the family (4.10). It is clear that the family (4.10) belongs to the class of functions (see eq. (2.11)), which satisfies

$$N[n] = \int n(\underline{z})\, d\underline{z} = N$$

Thus the variational principal of HK tells us that

$$\left(dE[n]/d\beta\right)_{\beta_0} = 0 \tag{4.12}$$

for the value of the parameter β_0 for which the family (4. 10) extremizes (4. 1). Or equivalently,

$$\left(\partial \nabla / \partial \beta\right)_{\beta_0} = 0 \tag{4. 13}$$

To evaluate equation (4. 13), one must first find $\nabla(\beta)$. Quite straightforwardly, one finds

$$\int_{-\infty}^{\infty} \partial z \left(\frac{3}{10}\right)\left(3\pi^2\right)^{2/3}\left(n^{5/3} - n_+^{5/3}\delta\right) = -3/10 \frac{\left(3\pi^2\right)^{2/3}}{\beta} n_+^{5/3}\left(.7926 - \frac{.6}{2^{5/3}}\right)$$

$$\int_{-\infty}^{\infty} \frac{\left(n - n_+\delta\right)}{2} \varphi \, dz = \pi n_+^2 / 2\beta^3$$

$$1/72 \int_{-\infty}^{\infty} \frac{\left(dn/dz\right)^2}{n} dz = \beta \frac{n_+}{72} \ln 2$$

$$-3/4\left(\frac{3}{\pi}\right)^{1/3} \int_{-\infty}^{\infty} \left(n^{4/3} - n_+^{4/3}\delta\right) dz = \left(\frac{3}{\pi}\right)^{1/3} \frac{n_+^{4/3}}{\beta} \left(\frac{3}{4}\right)\left(.636 - \frac{3}{2^{10/3}}\right)$$

$$5.6 \times 10^{-2} \int_0^{\infty} \frac{n^{4/3} dz}{\left(7.9 \times 10^{-2} + n^{1/3}\right)} = + \frac{8.4 \times 10^{-2} n_+}{\beta}\left[a^2 - \frac{a}{2} + 1/3 + a^3 \ln\left(\frac{a}{a+1}\right)\right]$$

where $$a = \frac{z^{1/3}}{n_+^{1/3}} (7.9 \times 10^{-2})$$

Finding the rest of the correlation energy integral is not straightforward, so the following approximation is made: for $z < 0$,

$$\frac{5.6\times10^{-2} n_+^{4/3}}{7.9\times10^{-2} + n_+^{1/3}} - \frac{5.6\times10^{-2} n^{4/3}}{7.9\times10^{-2} + n^{1/3}} \simeq$$

$$\simeq \frac{5.6\times10^{-2}\left(\pi/3\right)^{1/3}(4/3)}{(7.9\times10^{-2} + n_+^{1/3})}\left[-\frac{3}{4}\left(\frac{3}{\pi}\right)^{1/3} n^{4/3} + \frac{3}{4}\left(\frac{3}{\pi}\right)^{1/3} n_+^{4/3}\right]$$

It is estimated that this approximation will lead to a correlation energy from the $Z < 0$ region which is too large by less than 18 percent. One can easily be convinced that this will not cause a significant error in β_o for any of the metals studied. It is even less important when one realizes that Wigner claimed an accuracy of only ±20 percent for his correlation energy formula. Thus,

$$\int_{-\infty}^{0}\left[\frac{5.6\times10^{-2} n_+^{4/3}}{(7.9\times10^{-2} + n_+^{1/3})} - \frac{5.6\times10^{-2} n^{4/3}}{(7.9\times10^{-2} + n^{4/3})}\right] dz =$$

$$= \frac{5.6\times10^{-2}}{7.9\times10^{-2} + n_+^{1/3}}\left(0.636 - \frac{3}{2^{10/3}}\right).$$

Combining the above equations, one obtains

$$\nabla = \frac{A(n_+)}{\beta} + \frac{B(n_+)}{\beta^3} + \beta C(n_+) \qquad (4.14)$$

where A, B, and C are known constants for each n_+ value. ($B = n_+^2/2$, $C = (n_+/72)\ln 2$). Combining equations (4.13) and (4.14), one has

$$\beta^2 = \frac{A + \sqrt{A^2 + 12CB}}{2C} \qquad (4.15)$$

Then from equations (4.11) and (4.9), one obtains

$$\varphi_e = \frac{4\pi n_+}{\beta^2} - \frac{(3\pi^2)^{2/3}}{2} n_+^{2/3} + \left(\frac{3}{\pi}\right)^{1/3} n_+^{1/3} + \frac{5.6\times10^{-2} n_+^{2/3} + 5.9\times10^{-3} n_+^{1/3}}{(7.9\times10^{-2} + n_+^{1/3})^2} \qquad (4.16)$$

The results for φ_e, the dipole barrier, β, $V^{(1)}$, and ∇ are given in the attached tables and graphs. In all cases except Cu and Au the number of valence electrons per atom was taken to be equal to the recommended atomic valence as given in most periodic tables. The number of valence electrons per atom for Cu and Au were taken to be equal to one, since they are known to be monovalent metals.

It is reiterated that the only empirical data made use of in this calculation is the atomic valence and the density of atoms in the solid.

Discussion of Results

Fortunately, there is one calculation available which does solve the Hartree Fock equations nearly self-consistently, and does include correlation energies in an ad hoc fashion.[2] Additionally, Bardeen uses the same model. Thus a good test of the statistical formulation is available. This comparison is provided in Table I. The uncorrected Wigner interpolation formula was used in the statistical theory for this comparison, since Bardeen used it. We see that the double layer moments without exchange and correlation energies and without correlation energies are larger than when these energies are included. This underscores the need to include these energies in such calculations. Note that our dipole barrier without correlation is very close to Bardeen's corresponding value, but that when correlation energies are added there is a difference of 0.38 eV. This is probably due in part to the method Bardeen used to include correlation energies. He himself[83] noted many years later that it greatly overestimates momentum dependence of the exchange correlation hole. Another reason for the difference is that Bardeen's method includes quantum oscillations, which lead[84] to a hump in the charge distribution which we don't obtain. This bump obviously leads to a lower dipole barrier. But, as supposed earlier, the differences are of the

same order as grain orientation effects. Surface energies were calculated in this work primarily to make a comparison with that obtained by Huntington[85] using Bardeen's potentials.[2] We see that although the methods used by Huntington in calculating the surface energy were somewhat different than ours, reasonable agreement was obtained nevertheless. Thus it appears that the statistical formulation of HK as used here is an adequate method for somewhat crude calculations of metal surface properties. Next let us compare our one-electron potential (Fig. 1), with Bardeen's potentials.[86] The comparison should be made for the potential going with electrons near the top of the Fermi distributions (his $\alpha = 1.0$), since that is what our potential describes. One can see that in general the results are agreeable, but that Bardeen's potential contains Friedel-like oscillations which we knew we would not have. Bardeen required his potentials to become asymptotic with the curve 1/4 z, which we have sketched in figure 1. This curve is to represent an image potential which all one-electron potentials have to go to at large distances from the metal. But there is an ambiguity in the choice of the origin of coordinates in plotting the image potential. This is because one does not really know where the classical "surface" is in relation to the last row of atoms. This and the fact that statistical schemes are inherently inaccurate in regions of vanishing density are the main reasons that the 1/4z curve does not approach $V^{(1)}$ as rapidly as

Bardeen's potentials. Although the aforementioned ambiguity exists, the 1/4z curves are included on the other $V^{(1)}$ plots mainly for scaling.

An aside must be made to correct a misconception existing in the literature. Juretsche has[87] supposedly examined an exchange potential proportional to our exchange potential, $-(3/\pi)^{1/3} n^{1/3}$, and found it to be lacking in the "surface" region. However, he used an electron distribution bounded by an infinitely high barrier. We have now shown that the introduction of this nonphysical and most extreme barrier was the cause of most of the disagreement. He also notes quite correctly that his potential could be produced by a uniformly charged sphere of the proper radius. He then evaluates the effective exchange charge for positions far outside the metal and in the "surface" region. He found, of course, that the exchange hole does not remain spherical about the position in question when this position is in the surface layer or far outside the metal He then concluded incorrectly that this meant that the exchange potential $-3/2(3/\pi)^{1/3} n^{1/3}$ would be incorrect in these regions. This interpretation is incorrect since of course the potential $-3/2(3/\pi)^{1/3} n^{1/3}$ can be produced by other than spherical effective charge distributions, i.e., there is no uniqueness theorem applicable to the type of effective charge distribution used to produce this potential. The real criteria is how n falls off with dis-

tance from the surface, and we have shown that this falloff is reasonable.

Now let us see (table II) how our scheme does in uncharted domains, i. e., in calculating work functions of the other metals. We see that the results for the alkali metals are higher than experiment, but in the same order relative to each other. Considering the crudeness of the model, the agreement is heartening. The values of surface energy are consistently lower than the experimental values, as expected. The one-electron potentials are plotted in units of $1/r_s$(r_s = S sphere radius), so that shapes can be compared and then a representative from each group of metals is plotted in atomic units so that absolute values can be compared. Only enough potentials are plotted to obtain a perspective of the results. Of course, if desired, n and $V^{(1)}$ can be plotted for all the metals using the analytic forms (4. 10) and (4. 11) and the β_0 values given in Table II.

The noble metals have work function values which are lower than experiment. But still generally the values have less than 25 percent error. The surface energies are even going negative at this point (for $n_+ \gtrsim 13\text{x}10^{-3}$), indicating clearly the general inapplicability of our method for calculating this quantity. Hence, we stopped including them in the results. The discrepancy is probably explained in the main by Herring's observation noted earlier.

Quite good agreement is obtained for the experimental and theoretical ϕ_e for the free electron metals of intermediate bulk densities, Mg and Al. We note also that the double layer values are becoming considerably larger.

Finally we come to the transition metals which are so studied in experimental surface physics but practically unconsidered in theoretical surface physics . Happily it appears that the earlier experimental observations[78, 79] were prophetic and that these metals do behave like free electron metals for calculation of electron work functions. Note the order is generally correct and that the values are rather close to experiment. Note also the extremely large dipole barriers.

So we see that the model gives reasonable values over bulk densities varying by a factor of 50. As mentioned earlier, this is extremely encouraging when one realizes that the total electron work function has been calculated for only one metal, Na.

Addenum

One cannot help but wonder how this bare surface model would fit into adsorption theory. That is, how would one proceed to describe a system of particles adsorbed on this "jellium" surface? It is suggested here that an analogue of the Wigner-Seitz cell method[15] be used. As spherical symmetry was assumed about an atomic nucleus in the bulk, cylindrical symmetry is assumed about an axis normal to

the jellium surface and through the nucleus of the adsorbed particle. Likewise, as physical quantities (charge density, potential, etc.), were assumed to have vanishing normal derivatives at the surface of the sphere, physical quantities are assumed to have vanishing normal derivatives at the surface of the cylinder which has a cross-sectional area equal to the average area per particle. Thus a regular array of adsorbed particles can be described in this model analogously to the description of the bulk arrays via the Wigner-Seitz polyhedron method.

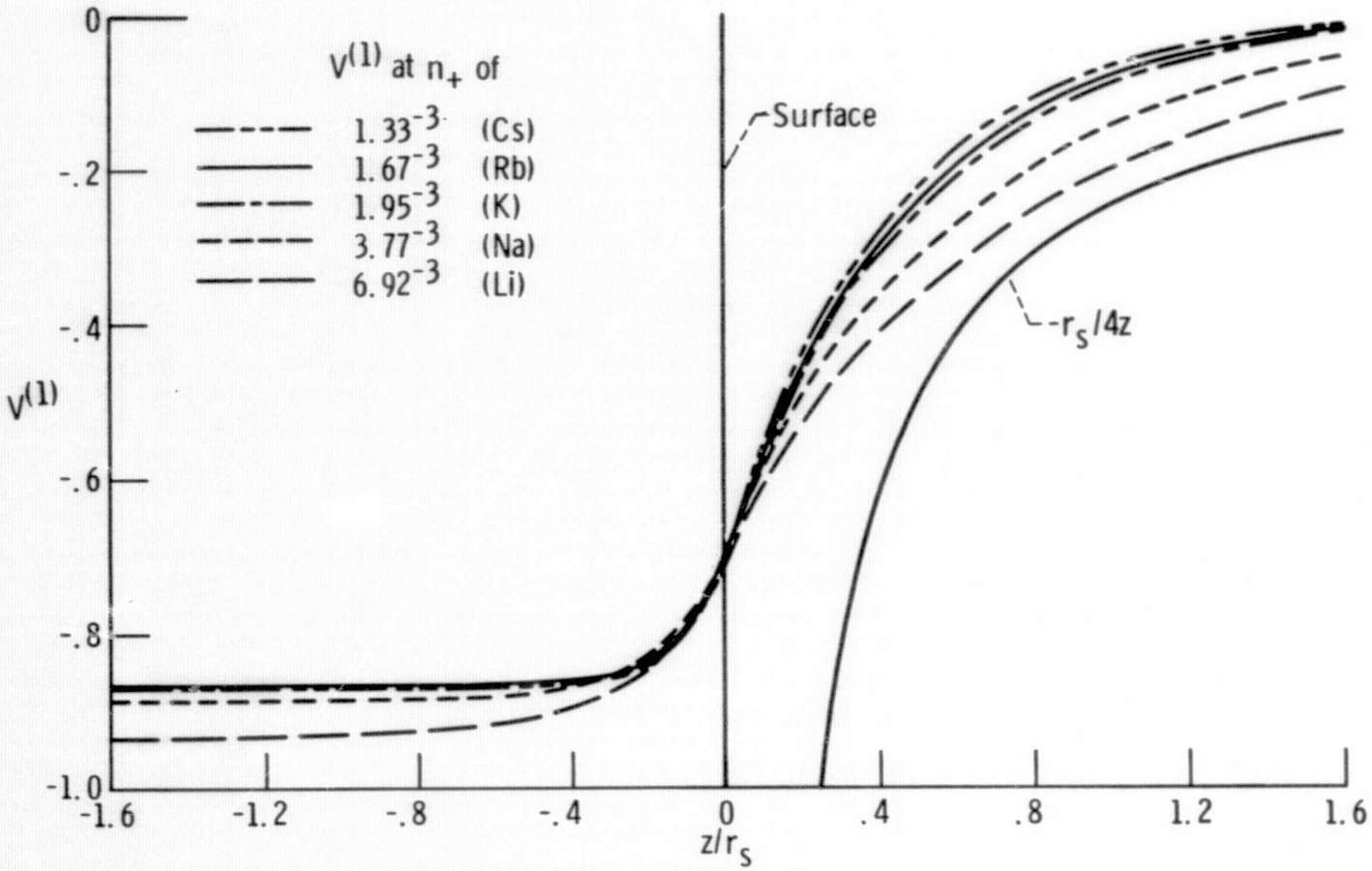

Figure 1. - $V^{(1)}$ in the surface region of the alkali metals in units of e^2/r_s.

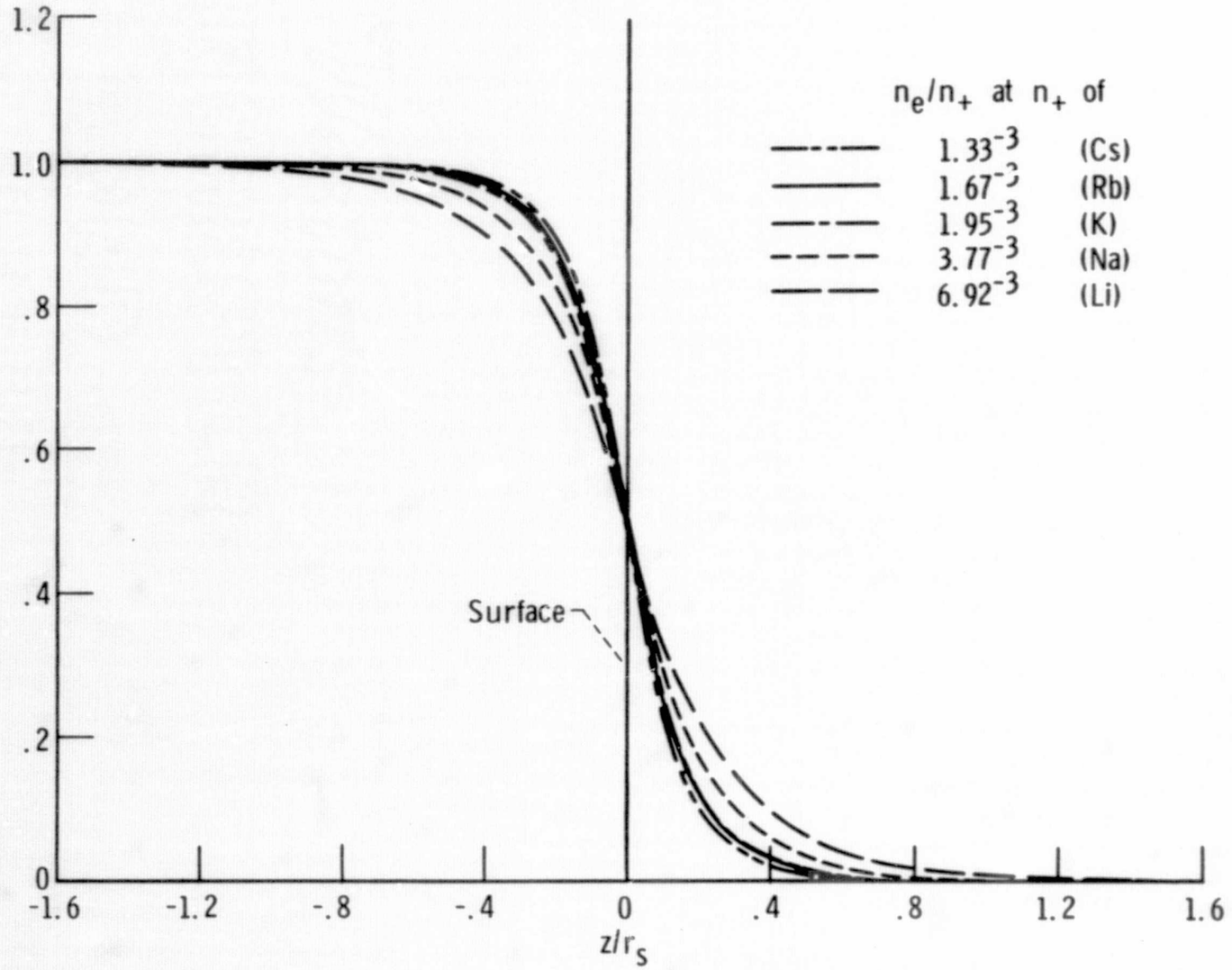

Figure 2. - Relative electron number density distribution in the surface region for the alkali metals.

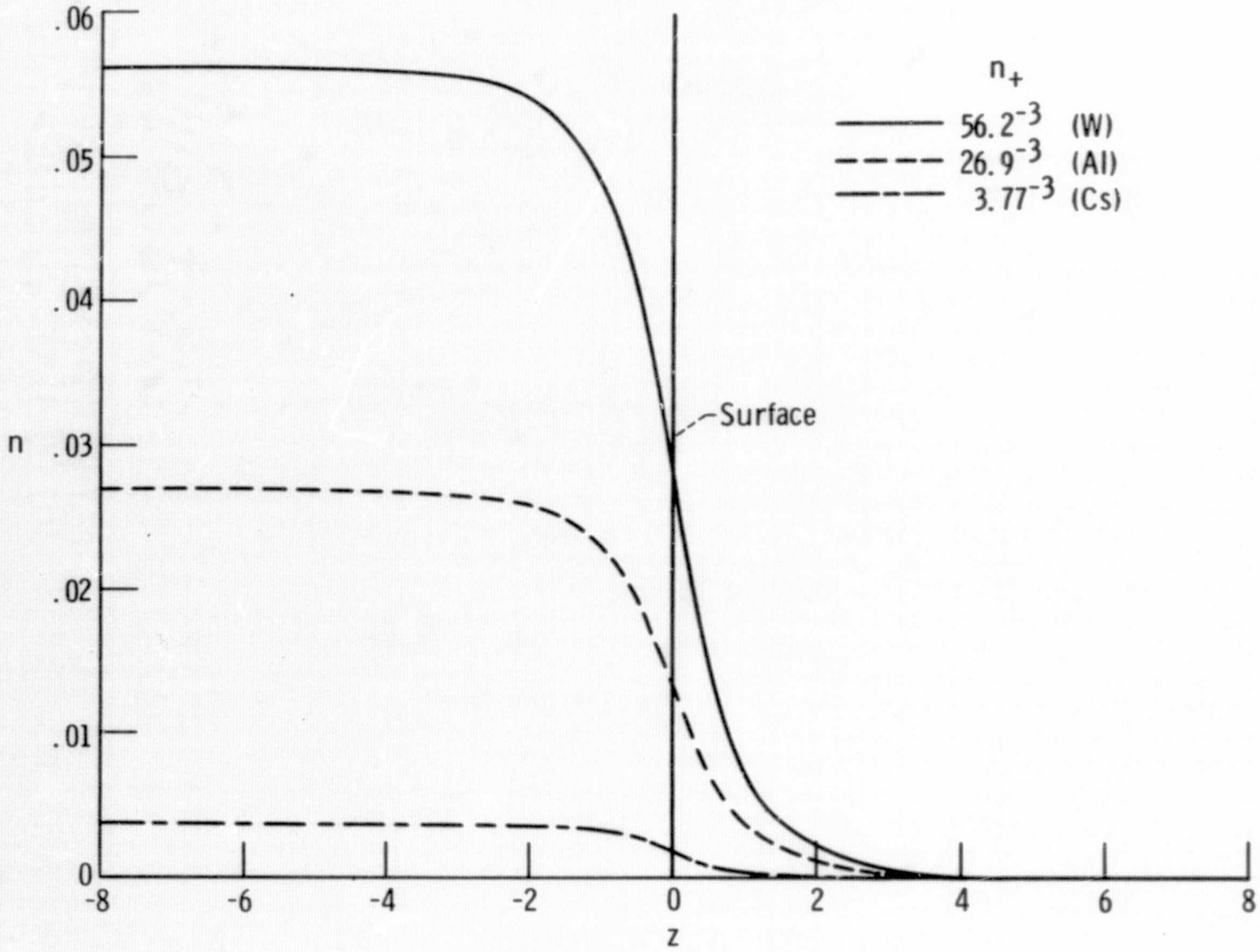

Figure 3. - Electron number density distributions in surface region for W, Al, and Cs using atomic units.

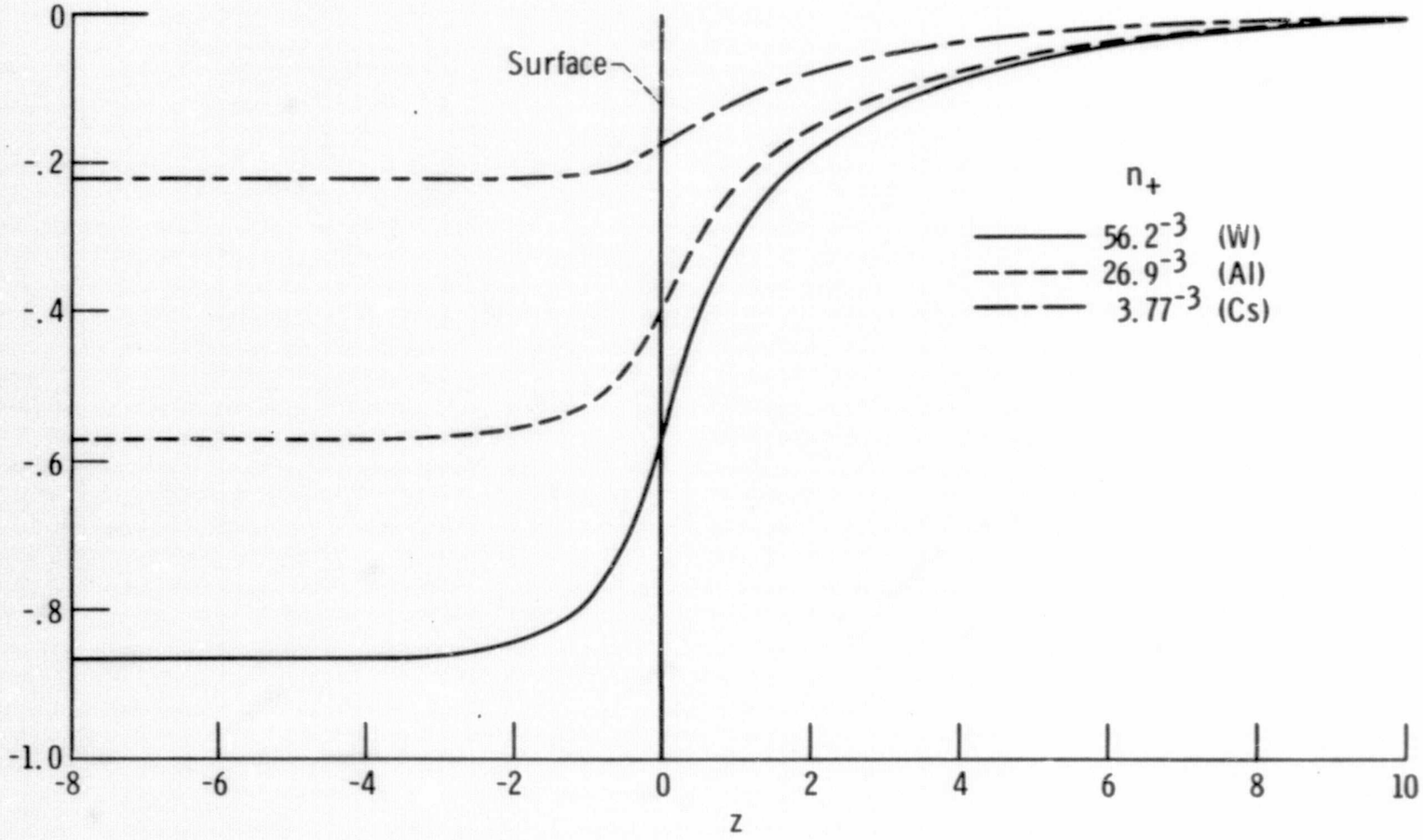

Figure 4. - $V^{(1)}$ in the surface region for W, Al, and Cs, using atomic units.

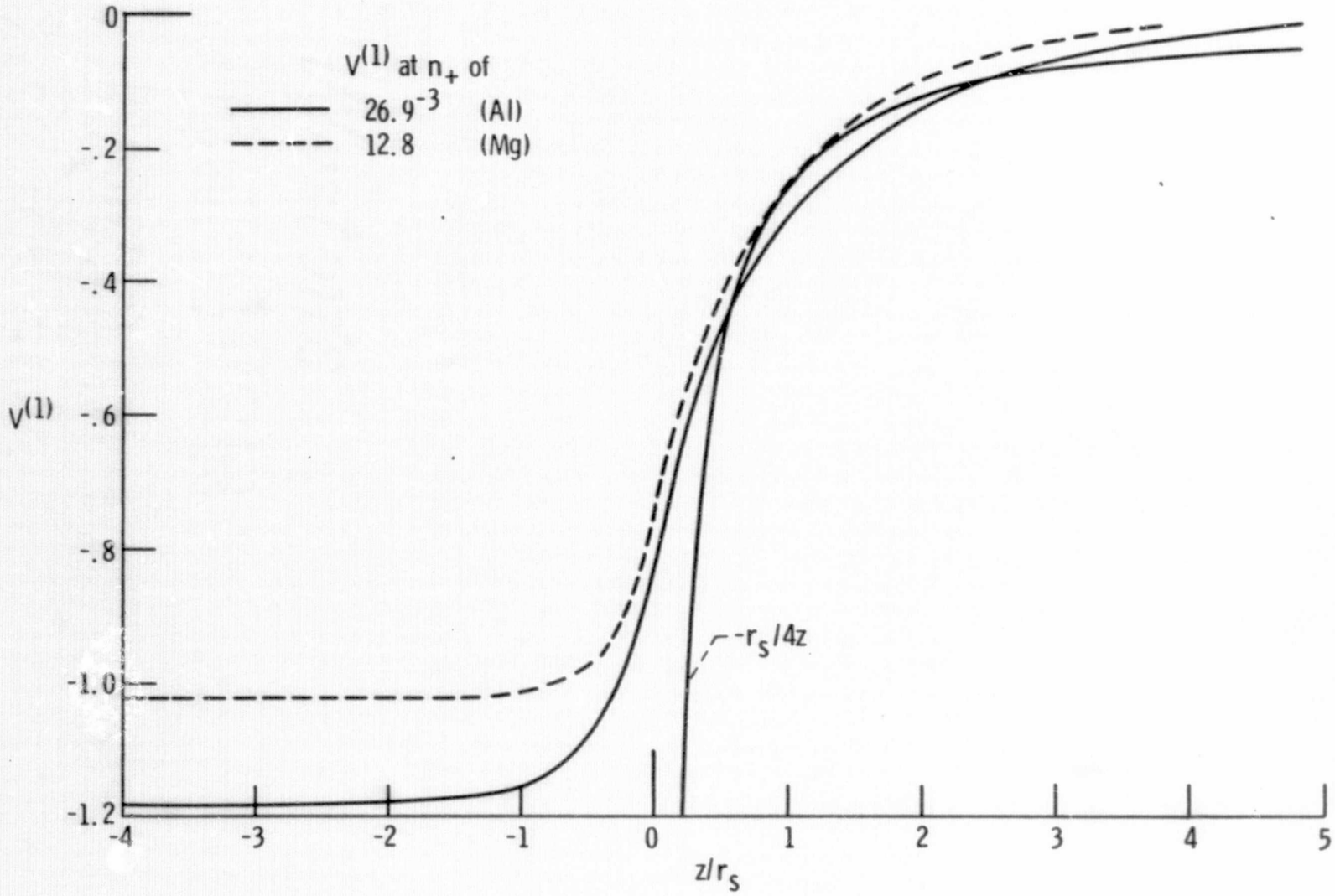

Figure 5. - $V^{(1)}$ in the surface region in units of e^2/r_s.

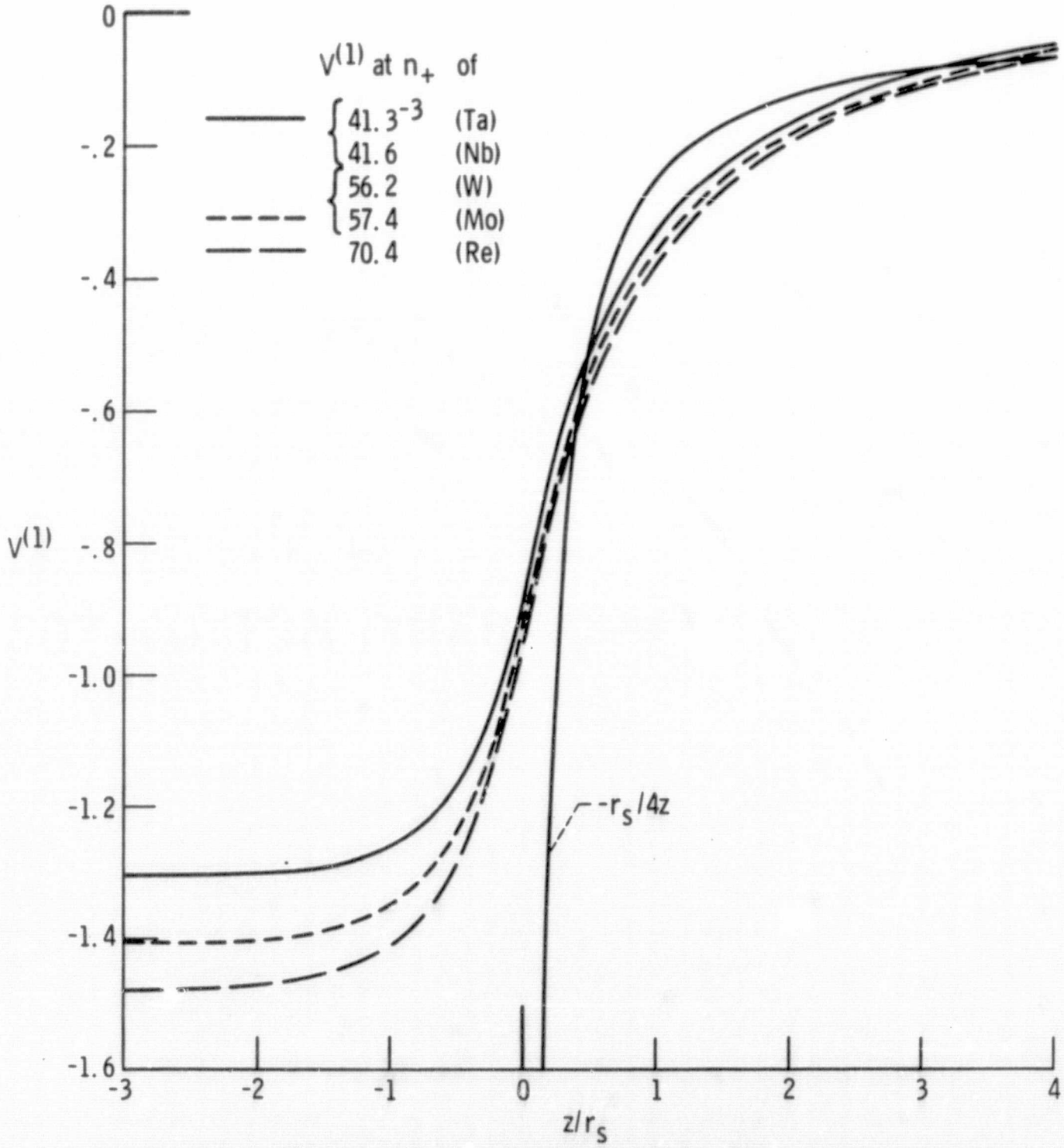

Figure 6. - $V^{(1)}$ in the surface region in units of e^2/r_s for selected refractory metals.

REFERENCES

1. V. S. Fomenko, "Handbook of Thermionic Properties", Plenum Press Data Division, New York (1966).
2. J. Bardeen, Phys. Rev. 49, 653 (1936).
3. G. V. Samsonov, et al., Sov. Phys.-Tech. Phys. 11, 1070 (1967).
4. L. N. Dobretsov, et al., Sov. Phys.-Tech. Phys. 11, 1081 (1967).
5. E. Wigner and J. Bardeen, Phys. Rev. 48, 84 (1935).
6. C. Herring, and M. Nichols, Rev. Mod. Phys. 21, 228-239 (1949).
7. W. Oldekop and F. Sauter, Zeitschrift für Physik 136, 534 (1954).
8. E. P. Wigner, Phys. Rev. 46, 1002 (1934).
9. T. Koopmans, Physica 1, 104 (1933).
10. R. Garron, Comptes Rendus 256, 2346 (1963).
11. M. Kaplit, Thermionic Conversion Specialist Conference, M.I.T., 387 (1966).
12. C. F. von Weizsäcker, Zeits. f. Physik 96, 431 (1935).

13. See, e.g., A. S. Kompaneets, et al., J.E.T.P. 4, 328 (1957).

14. M. Dubjko, et al., Phys. Stat. Sol. 16, 399 (1966).

15. E. Wigner and F. Seitz, Phys. Rev. 46, 509 (1933).

16. Ref. 6, pp. 244-54.

17. H. J. Juretschke, "The Surface Chemistry of Metals and Semiconductors," edited by H. Gatos, John Wiley & Sons, Inc., New York, p. 46 (1960).

18. J. Bardeen, Surface Science 2, 381 (1964).

19. J. Gerstner and P. H. Cutler, J. Phys. Chem. Solids 25, 105 (1964).

20. T. L. Loucks and P. H. Cutler, J. Phys. Chem. Solids 25, 105 (1964).

21. V. K. Semenchenko, "Surface Phenomena in Metals and Alloys," especially Chap. 2, 3, and 11, Addison-Wesley, Reading, Mass. (1962).

22. Y. Geguzin et al., Sov. Phys. Uspekhi 5, 129 (1962).

23. M. Inman, et al., Mett. Rev. 8, 105 (1963).

24. O. Flint, J. Nuclear Materials 16, 233 (1965).

25. Ref. 21, p. 388.

26. A. Skapski, Acta Met. 4, 576 (1956).

27. J. Taylor, Metallurgica 50, 161 (1954).

28. A. Sugiyama, J. Phys. Soc. of Japan 15, 965 (1960).

29. S. Zadumkin, Phys. of Metals and Metallography (S. S. S. R.) 11, (1960).

30. L. Thomas, Proc. Camb. Phil. Soc. 23, 542 (1927).

31. E. Fermi, Z. Phys. 48, 73 (1928).

32. N. March, Adv. in Phys. 6, 1 (1957).

33. P. Gombas, Handbuch der Physik 36, 109 (1956).

34. D. A. Kirshnits, JETP 5, 64 (1957).

35. G A. Baraff et al., Phys. Rev. 121, 1704 (1961).

36. P.A.M. Dirac, Proc. Cambridge Phil. Soc. 26, 376 (1930).

37. H. Schey et al., Phys. Rev. 137, A709 (1965).

38. N. N. Kalitkin, Sov. Phys.-JETP 11, 1106 (1960).

39. Ref. 34, pp. 68-9.

40. Y. Tomishima and K. Yonei, J. Phys. Soc. of Japan 21, 142 (1966).

41. H. W. Lewis, Phys Rev. 111, 1554 (1958).

42. D. F. DuBois and M. G. Kivelson, Phys. Rev. 127, 1182 (1962).

43. P. Hohenburg and W. Kohn, Phys. Rev. 136, B864 (1964).

44. W. J. Carr, Jr., and A. A. Maradudin, Phys. Rev. 133, A371 (1964).

45. P. Gombas, Acta Physica 13, 234 (1961).

46. Ref. 43, p. B868.

47. A. Erdelyi, "Asymptotic Expansion," Dover Pub., N. Y. (1956).

48. F. A. Kaempffer, "Concepts in Quantum Mechanics," A. P., New York, p. 222 (1965).

49. P. Gombas, Z. Phys. 121, 523 (1943).

50. V. A. Erma, Phys. Rev. 132, 1100 (1963).

51. W. Kohn and L. J. Sham, Phys. Rev. 140, A1133 (1965).

52. B. Y. Tong and L. J. Sham, Phys. Rev. 144, 1 (1966).

53. L. J. Sham and W. Kohn, Phys. Rev. 145, 561 (1966).

54. L. J. Sham, Phys. Rev. 150, 269 (1967).

55. J. F. Barnes, Phys. Rev. 153, 269 (1967).

56. N. Balazs, Phys. Rev. 156, 42 (1967).

57. See, e.g., M. Kaplit, et al., Adv. Energy Conv. 7, 177 (1966).

58. See, e.g., Ref. 50, fig. 1.

59. J. W. Sheldon, Phys. Rev. 99, 1291 (1955).

60. D. Pines, Solid State Physics 1, 374 (1955).

61. See, e.g., S. Raimes, "The Wave Mechanics of Electrons in Metals," Interscience Publishers Inc., New York (1961).

62. See equation 67 of Ref. 43.

63. L. Hulthen, Zs. f. Phys. 95, 789 (1935).

64. Ref. 59, p. 1295.

65. See, e.g., J. C. Slater, Phys. Rev. 81, 385 (1951).

66. Ref. 51, Appendix II.

67. Ref. 34, equation 27.

68. S. Ma and K. Brueckner, Phys. Rev. 165, 18 (1968).

69. J. Hubbard, Phys. Letters 25A, 709 (1967).

70. J. Hubbard, Proc. Roy. Soc. (London) A243, 336 (1957).

71. V. Fock, Phys. Z. Sowjet. 1, 747 (1932).

72. Ref. 51, p. A1134.

73. Ref. 13, p. 330.

74. C. Herring, in "Metal Interfaces." p. 117, American Society for Metals, 1952.

75. R. Smoluchowski, Phys. Rev. 60, 661 (1941).

76. C. H. Kelley, "The Kinetic Energy of Electrons Associated with the Line Boundary of a Two-Dimensional Crystal," (thesis), Poly. Inst. of Brooklyn, 1954.

77. P. Ewald and H. Juretschke, in "Structure and Properties of Solid Surfaces," edited by R. Gomer and C. Smith, The University of Chicago Press, Chicago, I11. (1953).

78. I. D'Haenens and E. Coomes, Phys. Rev. Letters 17, 516 (1966).

79. L. N. Thays and E. J. Scheibner, J. App. Phys. 38, 3320 (1967).

80. Ref. 74, p. 16.

81. Ref. 62, pp. 273-4.

82. Ref. 45, fig. 1.

83. Ref. 18, p. 385.

84. Ref. 2, fig. 5.

85. H. B. Huntington, Phys. Rev. 81, 1035 (1951).